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PROPELLANT/MATERIAL COMPATIBILITY STUDY

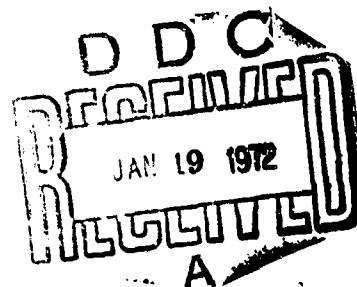
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AEROJET LIQUID ROCKET COMPANY

A Division of Aerojet-General Corporation

Technical Report AFRPL-TR-71-41

December 1971



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AIR FORCE SYSTEMS COMMAND
EDWARDS, CALIFORNIA



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SYNOPSIS

This report covers the work performed under Contract F04611-71-C-0004, "Propellant/Materials Compatibility Study", performed by the Aerojet Liquid Rocket Company at Sacramento, California, and conducted under Air Force Project 3148. The performance period covered from 1 September 1970 to 15 September 1971.

The project manager was Dr. S. D. Rosenberg; the project chemist was Dr. E. M. Vander Wall. The experimental work was conducted by Dr. Vander Wall; Dr. J. K. Suder, Chemistry Specialist; R. L. Beegle, Jr., Chemist; and J. A. Cabeal, Senior Laboratory Technician.

The program was administered under the direction of the Air Force Rocket Propulsion Laboratory, Lt Howard M. White, Project Engineer.

This report was submitted by the authors on 15 October 1971.

This technical report has been reviewed and is approved.

Howard M. White, 1st Lt, USAF
Project Engineer

ABSTRACT

The objective of this program was to define the threshold sensitivity limit of hydrazine fuels in common metallic materials of construction as a function of temperature and pressure. Four propellants were included in the program: hydrazine, monomethylhydrazine, MHF-5, and MHF-7. Eleven metallic materials of construction were included in the program: stainless steel 304L, 316, 321, 347, and 17-7PH; aluminum 1100-0, 6061-T6, and 2014-T6; Inconel-X 750; Haynes-25; and Hastelloy-X. Three standard tests were used to determine the threshold sensitivity limit of the propellants in the various materials: (1) thermal stability test, (2) detonation propagation test, and (3) U-tube adiabatic compression test.

The hydrazine, monomethylhydrazine, and MHF-7 were found to possess comparable thermal stability characteristics in the stainless steels, Inconel-X, Haynes-25, and Hastelloy-X, with less stability evident in the 2014-T6 and 6061-T6 aluminum alloys. The thermal stability temperature limits for MHF-5 were approximately 100°F lower than for the other fuels.

The detonation propagation tests demonstrated that the liquid phase of the fuels does not propagate a detonation in 0.9-in. internal diameter tubes at temperatures up to 400°F in hydrazine and monomethylhydrazine and up to 325°F in MHF-5.

Propellant/material interaction was apparent in the U-tube adiabatic compression tests. Under adiabatic compression conditions, the threshold temperature limit for explosive decomposition of hydrazine was 195°F to 217°F in 347SS, Haynes-25, 316SS, 321SS, Hastelloy-X, and 304LSS. The value dropped to 130°F for Inconel-X and 17-7PH, and the value dropped to less than 100°F for 2014-T6 and 6061-T6 aluminum. Monomethylhydrazine and MHF-7 were not sensitive to adiabatic compression to temperatures of at least 500°F; MHF-5 decomposed explosively under adiabatic compression at temperature levels approaching those at which explosive decomposition occurred in the thermal stability tests. The ability of small quantities of monomethylhydrazine to desensitize hydrazine vapor to adiabatic compression was dramatically demonstrated using 347SS, 304LSS, and 17-7PH with monomethylhydrazine concentration levels ranging from 2.5 to 10 weight percent in hydrazine. In addition, some confirmatory tests were conducted under thermal soak conditions to demonstrate the effect of materials under simulated thruster conditions.

All the tests were conducted with propellant-grade fuels and the materials were cleaned and passivated prior to testing.

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SECTION I

INTRODUCTION

Much effort has been directed toward the investigation of the stability and sensitivity of hydrazine fuels. Recently, the decomposition of hydrazine has been studied in detail under Contract F04611-67-C-0087 (Ref 1); the decomposition of monomethylhydrazine is being studied under Contract F04611-69-C-0096 (Ref 2 and 3); and the decomposition of hydrazine with various candidate bearing materials was evaluated under Contract F04611-68-C-0056 (Ref 4). However, none of these studies have considered the interrelated effects of shock and thermal stimuli together with material compatibility considerations. The purpose of the investigation which is discussed in this report was to define the threshold sensitivity limits of hydrazine fuels in common metals of construction as a function of temperature and pressure. The program was an extensive characterization of the fuels using accepted standard tests; and the results form a basis from which projected propulsion systems can be designed.

The investigation involves the use of four propellants: (1) hydrazine (2) monomethylhydrazine, (3) MHF-5, and (4) MHF-7. Eleven metallic materials of construction were included in the program:

Stainless steels 304L, 316, 321, 347, and 17-7PH

Aluminum 1100-0, 6061-T6, and 2014-T6

Inconel-X 750

Haynes-25

Hastelloy-X

Three standard tests were used to determine the threshold sensitivity limits of the propellants in the various materials:

Detonation propagation test

U-tube adiabatic compression test

Thermal stability test

Both the detonation propagation test and the U-tube adiabatic compression test are normally conducted at ambient temperatures, so the apparatus were modified sufficiently to allow testing at elevated temperatures.

SECTION II

EXPERIMENTAL RESULTS AND DISCUSSION

Prior to conducting the major test series in the program, preliminary tests were conducted to establish a suitable passivation procedure for the metals, and the propellants were formulated and analyzed to assure their conformance with the propellant specifications. The experimental results are presented under six headings: (A) Metal Pretreatment and Propellant Analyses, (B) U-Tube Adiabatic Compression Tests, (C) Thermal Stability Tests, (D) Detonation Propagation Tests, (E) Confirmatory Tests, and (F) Implications of Experimental Results.

A. METAL PRETREATMENT AND PROPELLANT ANALYSES

1. Pretreatment of Metals

Based on the experimental results of kinetic studies of the decomposition of hydrazine, there are three apparent mechanisms of decomposition that are significant from ambient to moderate (400°F) temperature levels: (1) a liquid-phase heterogeneous decomposition, (2) liquid-phase homogeneous decomposition which is apparently impurity-catalyzed, and (3) a vapor-phase heterogeneous reaction which may be inhibited by one of the products.

Factors affecting homogeneous decomposition rate are: (1) the purity of the hydrazine, (2) pretreatment of the hydrazine, (3) the cleaning and passivation procedures used for materials in contact with the hydrazine, and (4) the concentration of acidic species in the hydrazine. The liquid-phase homogeneous decomposition is considered to be either impurity-catalyzed or caused by a reactive impurity. In the latter case, the impurity is eventually consumed and the decomposition reaction ceases. Impurities which possess acidic characteristics in hydrazine are particularly effective in enhancing the decomposition reactions. The heterogeneous decomposition rates are dependent primarily on: (1) the container material involved and (2) the cleaning and passivation procedures used for the container material.

The scope of the program was limited to the use of propellants which comply with the propellant procurement specifications. No effort was made to reduce the concentration of impurities normally found in specification grade hydrazine fuels. Rather, emphasis was placed on the condition of the surface of the metallic materials. Therefore, two factors were addressed on the program: (1) selection of different material of construction; and (2) cleaning and passivation procedures for the selected materials. Note that these are the major factors involved in the heterogeneous decomposition mechanisms for hydrazine family of fuels.

In order to obtain valid data on the inherent effect of metals on the decomposition reactions of hydrazine fuels, it is essential to

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II, A, Metal Pretreatment and Propellant Analyses (cont.)

utilize the best cleaning and passivating procedures for each metal. Based on the decomposition mechanisms which are possible for hydrazine, the following cleaning and passivation procedures were used for the stainless steels, Inconel-X, Haynes-25, and Hastelloy-X.

- Step 1. The material was washed with trichloroethylene to remove organic residues.
- Step 2. The material was immersed in an aqueous pickling solution containing 28% nitric acid and 2% hydrofluoric acid. The minimum exposure times were 4 hours for the stainless steels, 2 hours for the Inconel-X and the Haynes-25, and 15 minutes for the Hastelloy-X.
- Step 3. The materials were flushed and rinsed thoroughly three times with distilled water to remove the acidic pickling solution and any solid residues.
- Step 4. The materials were then passivated in a 50% aqueous hydrazine solution for a minimum of 16 hours.
- Step 5. The materials were flushed and rinsed three times with distilled water to remove the hydrazine and residuals.
- Step 6. The materials were dried by purging in dry, filtered nitrogen and stored in nitrogen until used.

The aluminum materials were treated in the following manner:

- Step 1. The as-received materials were scrubbed with an aqueous detergent solution.
- Step 2. The materials were thoroughly flushed and rinsed with distilled water.
- Step 3. The materials were passivated in a 50% aqueous hydrazine solution for a minimum of 1 hour.
- Step 4. The materials were dried by purging with dry, filtered nitrogen and stored in nitrogen until used.

II, A, Metal Pretreatment and Propellant Analyses (cont.)

In Step 3 of the procedure for aluminum, the aqueous hydrazine acts as both the pickling solution and the passivating solution. The effectiveness of the pretreatment procedures was evaluated by two series of tests: Thermal stability and U-tube compression. The results were as follows:

Thermal stability tests were conducted in the 304L stainless steel bombs with hydrazine as the propellant. The first bomb was cleaned with trichloroethylene to remove adherent organic substances, then thoroughly rinsed with water and dried. The second bomb was cleaned using the previously described cleaning and passivating procedure. During the initial tests, the filling procedure was conducted in the air and, in the succeeding tests, the filling procedure was conducted in a controlled atmosphere box filled with nitrogen. The results are presented in Table I.

TABLE I

EFFECT OF PRETREATMENT OF 304L BOMB ON THERMAL STABILITY OF N_2H_4

	Start of Exotherm, °F	Burst Disc Rupture, °F	
N_2H_4 /Air	460	520	Passivated Bomb
N_2H_4 /Air	450	522	Unpassivated Bomb
N_2H_4 / N_2	480	528	Passivated Bomb
N_2H_4 / N_2	470	520	Unpassivated Bomb

Although the data show that the exotherm due to hydrazine decomposition occurred 10°F lower in the unpassivated bomb than in the passivated bomb, the temperature differences for the explosive decomposition reaction as noted by rupture of the burst disc is not as great. The results were considered inconclusive as far as the effectiveness of the passivation treatment is concerned and additional evaluation was conducted with the U-tube sensitivity tests.

The U-tube sensitivity tests were conducted in the adiabatic compression apparatus which is described in Section II,B. Although the valve was designed to completely open within 5 milliseconds, during the initial series of experiments, the valve required 15 milliseconds for complete opening. Based on later information, the slower valve-opening rate was inadequate for completely adiabatic compression, but the tests did demonstrate that the passivation treatment did increase the threshold temperature level for explosive decomposition. The results using 304L stainless steel are presented in Table II. The positive tests in which the tubes ruptured are indicated by a + sign and the negative tests in which the U-tubes survived are designated by a - sign. The tubes specified as "passivated" were subjected to the

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II, A, Metal Pretreatment and Propellant Analyses (cont.)

described cleaning and passivating procedure. The tubes specified as "unpassivated" were cleaned with trichloroethylene, then thoroughly rinsed with water and dried.

TABLE II

DATA INDICATIVE OF THE SENSITIVITY OF HYDRAZINE TO
COMPRESSION IN 304L STAINLESS STEEL AT ELEVATED TEMPERATURES

<u>Temperature,</u> <u>°F</u>	<u>Driving</u> <u>Pressure,</u> <u>psia</u>	<u>Ullage</u> <u>Gas</u>	<u>Result</u>	<u>Tube</u> <u>Condition</u>
414	1000	N ₂	+	Passivated
411	2000	N ₂	+	Passivated
401	2000	N ₂	+	Passivated
401	2000	N ₂	-	Passivated
395	2000	N ₂	-	Passivated
393	2000	N ₂	-	Passivated
392	2000	N ₂	-	Passivated
380	2000	N ₂	-	Passivated
414	1000	Air	+	Passivated
392	2000	Air	-	Passivated
389	2000	N ₂	+	Unpassivated
382	2000	N ₂	Spontaneous Decomposition	Unpassivated
379	2000	N ₂	+	Unpassivated
368	2000	N ₂	-	Unpassivated
366	2000	N ₂	-	Unpassivated

The significant items to be noted from the data are: (1) in the passivated 304L stainless steel tubes, the threshold level for sensitivity of hydrazine is between 395 and 401°F; (2) passivation of the tubing does increase the threshold temperature of sensitivity significantly (20°F); and (3) air does not significantly affect the threshold temperature level, perhaps due to the possibility that, during the heating cycle, the oxygen in the air may already have reacted with the hydrazine vapor.

II, A, Metal Pretreatment and Propellant Analyses (cont.)

2. Propellant Analyses

The hydrazine and monomethylhydrazine used in the program were used in the as-received condition with adequate precautions taken to avoid exposure to air. The hydrazine was analyzed in accordance with Specification MIL-P-26536C and the results are presented in Table III.

TABLE III

DATA INDICATIVE OF THE CONFORMANCE OF
THE HYDRAZINE WITH THE PROPELLANT SPECIFICATION

<u>Component or Property</u>	<u>Analysis Value</u>	<u>Specification MIL-P-26536C</u>
N_2H_4	99.45%	98% minimum
H_2O	0.24%	1.5% maximum
Density @ 77°F	1.004 g/ml	1.002 - 1.008 g/ml
Particulate matter	<1 mg/l	10 mg/l, maximum

A vapor chromatographic analysis of the same material indicated 99.7% N_2H_4 and 0.2% H_2O . The apparent dielectric constant of the hydrazine was determined using the Sargent Oscillometer at a frequency of 5 MHz and the value was found to be $\epsilon = 45.5$, which corresponds to hydrazine with less than 5 parts per million of carbon dioxide. This value indicates that the hydrazine has not been exposed to air for any significant period of time.

The monomethylhydrazine was analyzed in accordance with Specification MIL-P-27404A and the results are presented in Table IV.

TABLE IV

DATA INDICATIVE OF THE CONFORMANCE OF THE
MONOMETHYLHYDRAZINE WITH THE PROPELLANT SPECIFICATION

<u>Component or Property</u>	<u>Analysis Value</u>	<u>Specification MIL-P-27404A</u>
$CH_3N_2H_3$	99.74%	98.3% minimum
H_2O	0.2%	1.5% maximum
Density @ 77°F	0.870 g/ml	0.870 - 0.874 g/ml
Particulate matter	3 ppm	10 ppm maximum

The dielectric constant was measured with the Sargent Oscillometer and the value was found to be $\epsilon = 19$, which agrees with the literature data for monomethylhydrazine.

II, A, Metal Pretreatment and Propellant Analyses (cont.)

The MHF-5 was formulated on a gravimetric basis to meet Specification MIL-P-81507(AS). The hydrazine and monomethylhydrazine were used from the analyzed supply described above and the hydrazine nitrate required for the preparation was purchased* and shipped under methanol. Prior to formulation, the hydrazine nitrate was dried under vacuum to remove the methanol.

The MHF-7 was formulated on a gravimetric basis using the analyzed hydrazine, analyzed monomethylhydrazine, and distilled water. The composition used was 81% MMH, 14% N_2H_4 , and 5% H_2O . The nominal composition for MHF-7 is 81 ± 4 wt% MMH, 14 ± 3 wt% N_2H_4 , and 5 ± 1 wt% H_2O .

B. U-TUBE ADIABATIC COMPRESSION TESTS

The purpose of the U-tube adiabatic compression tests is to determine the behavior of the propellant liquid and vapor with the selected materials under simultaneous thermal and shock stimuli. The discussion in this section is presented under four headings: (1) Apparatus and Procedures, (2) Experimental Results, (3) Summation of the Results with N_2H_4 , MMH, MHF-5, and MHF-7, and (4) Effect of the MMH Concentration on the Sensitivity of N_2H_4 to Adiabatic Compression.

1. Apparatus and Procedures

A schematic drawing of the apparatus is shown in Figure 1 and a photograph is shown in Figure 2. The apparatus consists of a high-pressure spherical tank which is pressurized to the desired driving pressure with gaseous nitrogen. The tank is connected to the U-tube containing the test propellant through a rapid-opening valve, a check valve, and burst disc assembly. The burst discs were made of 304L stainless steel. The opening time for the valve was less than 5 msec, which provided a pressurization rate of 300,000 psi/sec or greater. The purpose of the check valve was to protect the relatively expensive high-speed valve from damage during the tests. The burst disc served two purposes: (1) to prevent propellant vapors from collecting in the check valve; and (2) to allow the propellant temperature to equilibrate with the oil bath temperature by preventing refluxing of the liquid above the bath level. The U-tube (0.35 in. wall thickness) containing the propellant was heated to the desired temperature by raising an oil bath so that the entire U-tube up to the burst disc assembly was heated to the desired temperature. The temperature of the bath was monitored by means of a thermocouple. The bath was raised and lowered by means of a remotely controlled power-jack which lifted the oil bath out of a protective sleeve during the heating cycle, then lowered the bath back into the protective sleeve after the propellant was heated. A cover over the oil bath was pulled into

*Purchased from Hummel Chemical Company, Inc., South Plainfield, New Jersey.

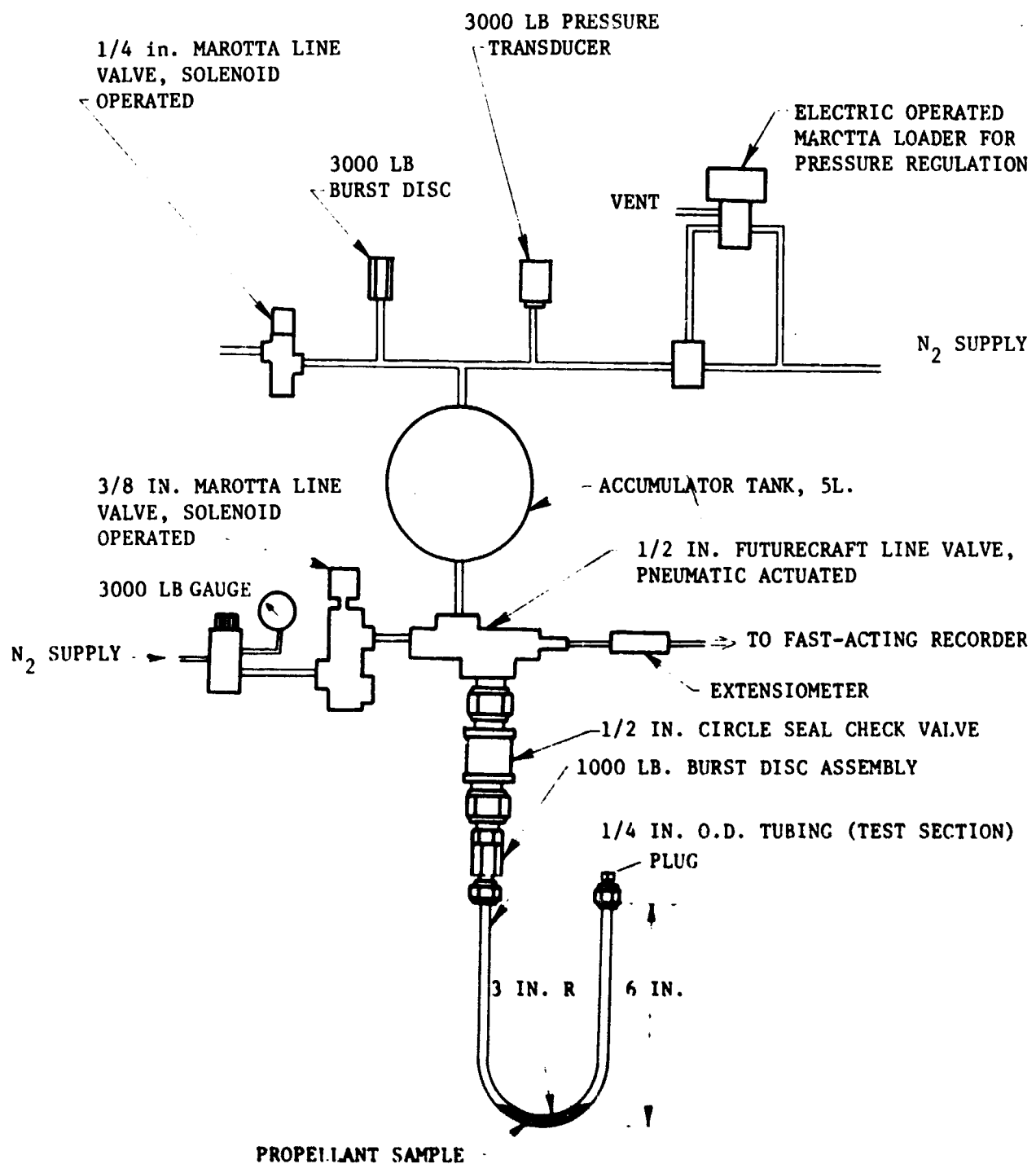


Figure 1. Schematic Diagram of U-Tube Adiabatic Compression Apparatus

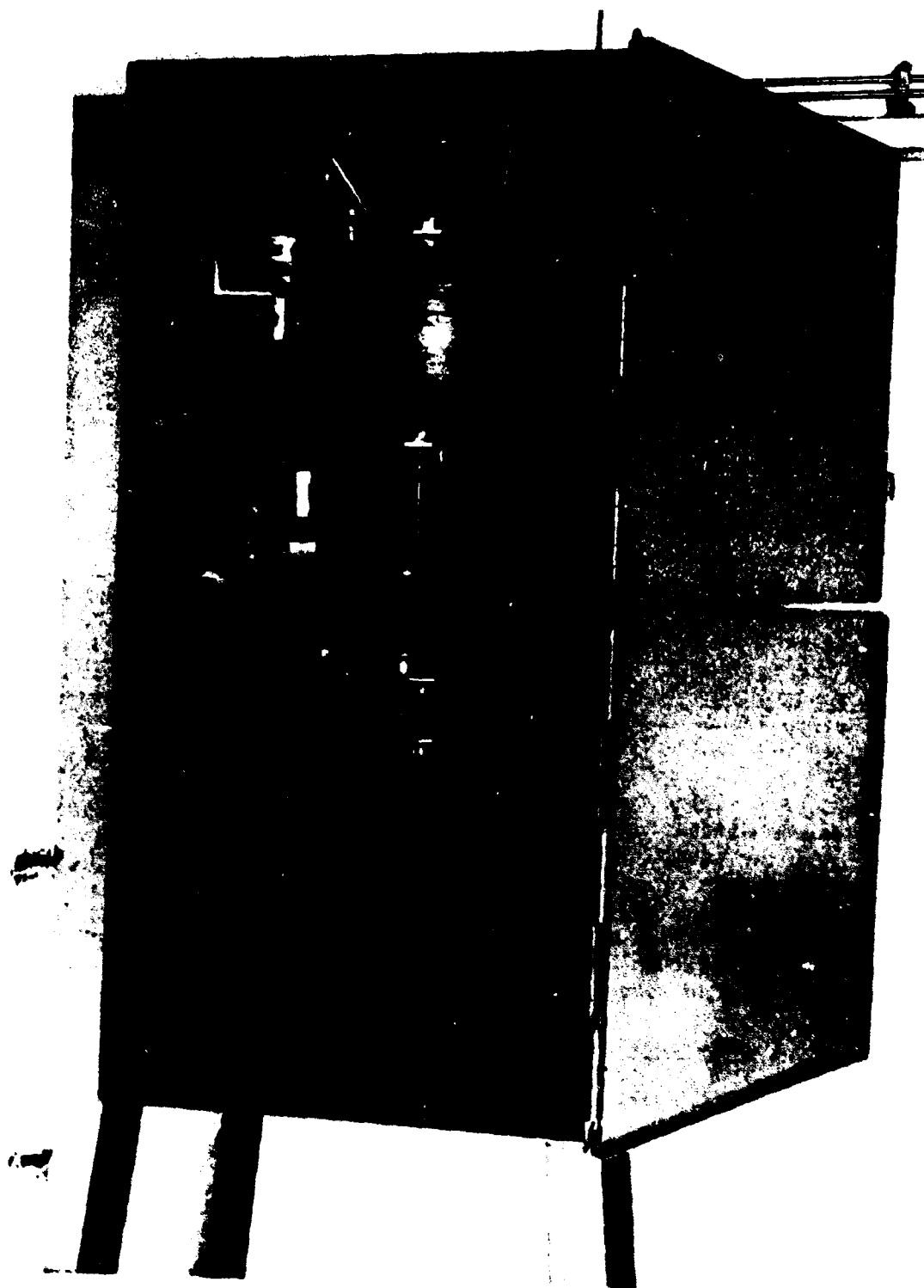


Figure 2. U-Tube Adiabatic Compression Test Apparatus

II, B, U-Tube Adiabatic Compression Tests (cont.)

place by a mechanical linkage to minimize oil spillage. Calibration tests with water indicated that thermal equilibrium between the bath and the contents of the stainless steel tubes was achieved within five minutes after immersion of the tube in the bath.

The normal procedure for the tests was as follows. The cleaned and passivated U-tube was loaded in a dry nitrogen atmosphere with 3 ml of the desired propellant. The tube was capped at both ends and then transferred to the test apparatus to avoid contamination by air. The U-tube was connected to the burst disc assembly of the apparatus. When the bath reached the desired temperature level, the bath was raised into position and the tube remained immersed for five minutes to allow equilibration. During this period, the accumulator tank was pressurized to the desired level, normally 2000 psig. The bath was then lowered and the valve immediately opened.

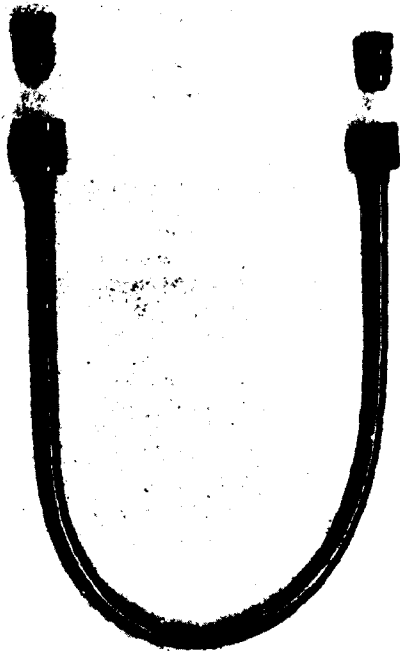
If the U-tube ruptured, the temperature was lowered 5 to 10°F for the next test; if the U-tube survived the test, the temperature was raised 5 to 10°F. This sequence was repeated several times and the temperature level below which no U-tubes were destroyed is defined as the threshold temperature limit for sensitivity to adiabatic compression. As the testing progressed, it became apparent that the number of tests with monomethylhydrazine, MHF-7, MHF-5, and the various materials could be minimized because of the insensitivity of monomethylhydrazine vapor to adiabatic compression. In the aforementioned propellants, monomethylhydrazine is the predominant vapor component.

The results of the tests were designated as either positive or negative. A positive result was one in which the tube was ruptured by an explosive decomposition; either the tube was entirely severed or fragments were torn from the tube. A negative result was one in which the tube survives the test intact or one in which only a split occurs due to overpressurization from a reaction. Typical tubes are shown in Figure 3. In cases in which the over-pressurization occurred, it was found that an increase in the initial liquid temperature of less than 10°F led to the separation of fragments from the tube in subsequent tests.

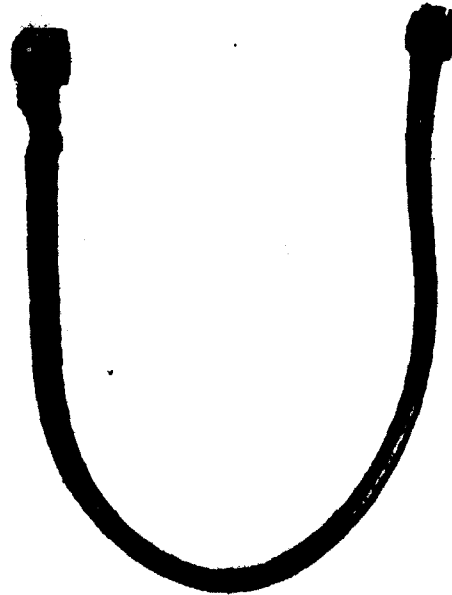
2. Experimental Results

a. Hydrazine

The threshold temperature limits for sensitivity of hydrazine to adiabatic compression in the selected materials were determined in accordance with the described procedures. The driving pressure for the tests was normally 2000 psig and the compression ratio was determined by the vapor pressure of the hydrazine and the nitrogen atmosphere initially present in the tube. For example, at 200°F, the total pressure with hydrazine in the tube is 25.5 psia and the compression ratio is 79:1; at 300°F, the total



EXAMPLE OF AN U-TUBE



EXAMPLE OF A POSITIVE TEST -
A FRAGMENT SEVERED



Figure 3. Examples of U-Tubes Employed in Tests

II, B, U-Tube Adiabatic Compression Tests (cont.)

pressure is 63 psia with hydrazine in tube and the compression ratio is 32:1. The data obtained with the stainless steel U-tubes are presented in Table V. The positive tests in which the tubes ruptured are designated by a + sign; the negative tests in which the U-tube survived the tests are designated by a - sign. The temperature value is that of the liquid sample prior to actuating the pressurization valve.

The data obtained with the Inconel-X, Haynes-25, Hastelloy-X, and aluminum alloy tubes are presented in Table VI.

The threshold temperature limits for sensitivity of hydrazine to adiabatic compression as derived from the preceding data are summarized in Table VII.

There is a significant difference in the temperature limits of sensitivity between the 17-7PH and the other stainless steels which were evaluated. The cause for the apparent catalytic effect was not identified in this program. Inconel-X exhibits a behavior similar to that of the 17-7PH, while the Haynes-25 and Hastelloy-X behave in a manner similar to that of the austenitic stainless steels. The effect of variation between lots of the same alloy is shown by the range for the threshold temperature limit of the 304L stainless steel. The 1100-0 aluminum could not withstand the adiabatic compression test at 68°F using water instead of the hydrazine. The 2014-T6 aluminum tubes were found to withstand the adiabatic compression test with water or monomethylhydrazine to 300°F; the 6061-T6 aluminum tubes withstood testing with water to 166°F.

TABLE V

DATA INDICATIVE OF THE SENSITIVITY OF HYDRAZINE TO ADIABATIC
COMPRESSION IN STAINLESS STEELS AT ELEVATED TEMPERATURES

304L Lot No. 1		304L Lot No. 2		316		321		347		17-7PH	
Temp, °F	Result	Temp, °F	Result	Temp, °F	Result	Temp, °F	Result	Temp, °F	Result	Temp, °F	Result
360	+	212	+	212	+	364	+	285	+	202	+
317	+	212	+	212	-	340	+	273	+	189	+
239	+	200	+	212	+	327	+	271	-	181	+
233	+	195	+	205	-	312	+	265	+	178	-
224	+	195	-	205	-	303	+	232	+	173	+
222	+	190	-	205	+	290	+	210	+	172	+
219	+	190	-	205	-	281	+	207	+	169	+
217	-			205	-	270	-	206	+	161	+
214	-			200	-	269	+	196	-	159	+
207	-			200	-	265	+	172	-	149	+
200	-			200	-	261	+	152	-	142	+
198	-			200	-	215	+			141	-
187	-					213	-			136	-
174	-					210	-			134	-
154	-					172	-			132	+
						155	-			124	-
										121	-
										72	-

TABLE VI

DATA INDICATIVE OF THE SENSITIVITY OF HYDRAZINE TO ADIABATIC COMPRESSION IN
INCONEL-X, HAYNES-25, 6061-T6 AND 2014-T6 ALUMINUM AT ELEVATED TEMPERATURES

Inconel-X		Haynes-25		Hastelloy-X		2014-T6 Aluminum		6061-T6 Aluminum	
Temp, °F	Result	Temp, °F	Result	Temp, °F	Result	Temp, °F	Result	Temp, °F	Result
161	+	234	+	220	+	210	+	257	+
153	+	217	-	212	+	198	+	123	+
142	-	212	+	212	-	105	+	114	+
135	-	207	+	212	-	98	+	92	+
133	+	205	+	212	+	95	+	84	+
127	-	204	-	212	-	88	-	74	+
122	-	202	-	212	+	80	-	68	-
		194	-	212	-	68	-	68	-
		191	-	212	-	52	-		
		188	-	212	-				
		181	-	212	-				
		178	-	212	-				
		164	-	205	-				
		139	-	205	-				
				200	-				
				200	-				
				200	-				

TABLE VIITHRESHOLD TEMPERATURE LIMITS FOR SENSITIVITY OF HYDRAZINE TO
ADIABATIC COMPRESSION IN SELECTED MATERIALS

<u>Material</u>	<u>Temperature, °F</u>
304L stainless steel	195 to 215
316 stainless steel	205
321 stainless steel	210
347 stainless steel	~200
17-7PH stainless steel	~130
Inconel-X	~130
Haynes-25	205
Hastelloy-X	210
2014-T6 aluminum	~90
6061-T6 aluminum	<68

b. Monomethylhydrazine

The threshold temperature limits for the sensitivity of monomethylhydrazine to adiabatic compression in the selected materials were determined by the same procedures as those used for hydrazine. The driving pressure for the tests was higher than that used for hydrazine because the vapor pressure of monomethylhydrazine is greater than that of hydrazine at the same temperature. The compression ratio values ranged from 4 to 33 during these experiments. The data obtained with the various metals are presented in Table VIII.

The significant item to be noted from the data is that none of the tubes were ruptured during the tests. The insensitivity of monomethylhydrazine vapor to adiabatic compression is dramatically demonstrated by the tests.

Based on the data presented in Table VIII, the threshold temperature limits for the sensitivity of monomethylhydrazine to adiabatic compression were assigned and the lower limit values are summarized in Table IX.

TABLE VIII

DATA INDICATIVE OF THE SENSITIVITY OF MONOMETHYLHYDRAZINE TO
ADIABATIC COMPRESSION IN THE SELECTED MATERIALS AT ELEVATED TEMPERATURES

<u>Material</u>	<u>Initial Liquid Temperature, °F</u>	<u>Driving Pressure, psig</u>	<u>Result</u>
304L SS	512	3000	-
304L SS	506	3000	-
304L SS	503	2000	-
304L SS	469	2000	-
304L SS	437	2000	-
304L SS	409	2000	-
304L SS	399	2000	-
304L SS	380	2000	-
316 SS	450	2800	-
316 SS	450	2800	-
316 SS	450	2800	-
321 SS	512	3000	-
321 SS	394	2000	-
321 SS	345	2000	-
321 SS	212	1500	-
321 SS	212	1500	-
347 SS	504	3000	-
347 SS	400	2000	-
347 SS	344	2000	-
347 SS	212	1500	-
17-7PH	486	2500	-
17-7PH	485	2500	-
Inconel-X	481	2500	-
Inconel-X	468	2000	-
Inconel-X	401	2000	-
Inconel-X	297	2000	-
Haynes-25	512	3000	-
Haynes-25	502	3000	-
Haynes-25	484	3000	-
Hastelloy-X	475	3000	-
Hastelloy-X	475	3000	-
Hastelloy-X	470	3000	-
2014-T6 Al	300	2000	-
2014-T6 Al	212	2000	-
6061-T6 Al	155	2000	-

II, B, U-Tube Adiabatic Compression Tests (cont.)

TABLE IXTHRESHOLD TEMPERATURE LIMITS FOR SENSITIVITY OF MONOMETHYLHYDRAZINE
TO ADIABATIC COMPRESSION IN SELECTED MATERIALS

<u>Material</u>	<u>Temperature, °F</u>
304L stainless steel	>512
316 stainless steel	>450
321 stainless steel	>512
347 stainless steel	>504
17-7PH stainless steel	>486
Inconel-X	>481
Haynes-25	>512
Hastelloy-X	>475
2014-T6 aluminum	>300
6061-T6 aluminum	>165

The tests were not continued at higher temperatures than those specified in Table IX because the rate of thermal decomposition of monomethylhydrazine becomes significant above these temperatures. In the case of the aluminum alloys, the temperature limit was imposed by the lack of structural integrity of the material at the elevated temperatures rather than the characteristics of the monomethylhydrazine itself.

c. MHF-7

The threshold temperature limits for the sensitivity of MHF-7 to adiabatic compression in the selected materials were determined by the described procedure. The driving pressure of the nitrogen used in the tests was always greater than 2000 psig so that a significant compression ratio would be attained during the test. The number of tests with MHF-7 was limited because the behavior was anticipated to be comparable to that of monomethylhydrazine itself. The data are presented in Table X.

The data demonstrate that MHF-7 behaves similarly to monomethylhydrazine under adiabatic compression at elevated temperatures; the vapors are not sensitive to the compression. The aluminum alloys were not used in the tests due to their lack of structural integrity at elevated temperatures.

II, B, U-Tube Adiabatic Compression Tests (cont.)

TABLE X

DATA INDICATIVE OF THE SENSITIVITY OF MHF-7 TO ADIABATIC
COMPRESSION IN THE SELECTED MATERIALS AT ELEVATED TEMPERATURES

<u>Material</u>	<u>Initial Liquid Temperature, °F</u>	<u>Driving Pressure, psia</u>	<u>Results</u>
304L SS	519	3000	-
304L SS	510	3000	-
316 SS	500	2800	-, -, -
321 SS	512	3000	-
347 SS	508	3000	-
17-7PH	483	2300	-
17-7PH	482	2300	-
Inconel-X	484	2500	-
Inconel-X	483	2500	-
Haynes-25	521	3000	-
Haynes-25	512	3000	-
Hastelloy-X	500	3000	-, -, -

d. MHF-5

The threshold temperature limits for the sensitivity of MHF-5 to adiabatic compression in selected materials were determined by the described procedure. The driving pressure of the nitrogen was maintained at or above 2000 psig to maintain a significant compression ratio during the test. The test results are presented in Table XI.

Based on the data presented in Table XI, the threshold temperature limits for the sensitivity of MHF-5 to adiabatic compression were assigned and the values are summarized in Table XII. The data in Table XII indicate that MHF-5 is much less sensitive to adiabatic compression than hydrazine; this is no doubt due to the presence of the monomethylhydrazine in the blend. The upper limit of the temperature values used in the tests were based on the thermal decomposition data for MHF-5 derived from the thermal stability tests. It would appear that the positive results during these tests are due to the initiation of the hydrazine nitrate decomposition process. The aluminum alloys were not evaluated in this test series because of their lack of structural strength at the elevated temperatures.

TABLE XI

DATA INDICATIVE OF THE SENSITIVITY OF MHF-5 TO ADIABATIC
COMPRESSION IN SELECTED MATERIALS AT ELEVATED TEMPERATURES

<u>Material</u>	<u>Initial Liquid Temperature, °F</u>	<u>Driving Pressure, psig</u>	<u>Results</u>
304L SS	461	3000	-
304L SS	443	3000	+
304L SS	436	3000	-
304L SS	433	3000	+
304L SS	432	2000	-
304L SS	425	3000	-
304L SS	404	3000	-
304L SS	367	2000	-
304L SS	286	2000	-
316 SS	400	3000	-
316 SS	400	3000	-
316 SS	400	3000	-
347 SS	463	3000	-
347 SS	457	3000	-
347 SS	462	2000	-
347 SS	442	2000	-
347 SS	426	2000	-
347 SS	415	2000	-
347 SS	381	2000	-
347 SS	367	2000	-
347 SS	353	2000	-
347 SS	340	2000	-
347 SS	328	2000	-
321 SS	460	3000	-
321 SS	444	2000	-
321 SS	351	2000	-
17-7PH	435	2200	-
17-7PH	438	2200	-
Inconel-X	430	2300	-
Inconel-X	430	2200	-
Haynes-25	417	3000	-
Haynes-25	412	3000	-
Haynes-25	409	3000	-
Haynes-25	390	3000	+
Haynes-25	386	3000	-
Haynes-25	384	3000	-
Haynes-25	376	3000	-
Haynes-25	372	3000	-
Hastelloy-X	350	2600	-
Hastelloy-X	350	3000	-,-,-,-
Hastelloy-X	362	2900	+

II, B, U-Tube Adiabatic Compression Tests (cont.)

TABLE XII

THRESHOLD TEMPERATURE LIMITS FOR SENSITIVITY OF MHF-5 TO
ADIABATIC COMPRESSION IN SELECTED MATERIALS

<u>Material</u>	<u>Temperature, °F</u>
304L stainless steel	430
316 stainless steel	>400
321 stainless steel	>460
347 stainless steel	>463
17-7PH stainless steel	>438
Inconel-X	>430
Haynes-25	385
Hastelloy-X	350

3. Summation of the Results with N_2H_4 , MMH, MHF-5, and MHF-7

The experimental data indicate that hydrazine/material interactions leading to the explosive decomposition of hydrazine do occur under adiabatic compression conditions with the vapor at elevated temperatures. The order of increasing reactivity in the metal alloys selected for study is 321 SS, Hastelloy-X, 316 SS, Haynes-25, 304L SS, 347 SS, < 17-7PH, Inconel-X < 2014-T6 Al < 6061-T6 Al. The aluminum alloy/hydrazine interaction may have been magnified in these tests because of the lack of structural integrity of the aluminum alloys at elevated temperatures.

The experimental data indicate that, although monomethylhydrazine/material interactions may occur under adiabatic compression conditions, the vapor does not undergo an explosive decomposition in the presence of liquid at initial temperatures approaching 500°F. This stability is in marked contrast to that of the hydrazine. Chemical analysis of the liquid phase of monomethylhydrazine after subjection to adiabatic compression at an initial liquid temperature of 480°F in Inconel-X and in 304L stainless steel indicated the presence of a trace of azomethane, $CH_3N = NCH_3$, in the sample from the Inconel-X tube and a significant quantity of azomethane in the sample from the 304L stainless steel tube. The presence of azomethane in the decomposition products of monomethylhydrazine has been previously reported by SRI in studies in which monomethylhydrazine was exposed to stainless steel, aluminum, and Inconel X-750 coupons in Pyrex glass for 7 days at 100°C. The azomethane formation was independent of the metal alloys present in the Pyrex glass tube (Ref 3 and 5).

II, B, U-Tube Adiabatic Compression Tests (cont.)

The presence of the monomethylhydrazine in the blends containing hydrazine has a very beneficial effect with regard to the decomposition that occurs during the adiabatic compression conditions. In tests with the MHF-7, no explosive decompositions occurred even though the temperatures of the liquid were raised to nominally 500°F before the adiabatic compression test. The monomethylhydrazine vapor evidently quenches the explosive decomposition of the hydrazine. Explosive decomposition occurs with hydrazine above 215°F in 321 stainless steel with a hydrazine vapor pressure of 10 psia. In MHF-7 at 500°F, the calculated partial pressure of hydrazine is 80 psia and no explosive decomposition occurs in 321 stainless steel.

The stabilizing influence of the monomethylhydrazine vapor is also evident in the MHF-5 tests. The explosive decompositions do not occur below 350°F and then only in the Haynes-25 and Hastelloy-X at temperatures below 400°F. The explosive decompositions which did occur with the MHF-5 may have been initiated by the hydrazine nitrate decomposition rather than a vapor decomposition reaction.

The adiabatic compression tests demonstrate that hydrazine/material interactions under simultaneous thermal and shock stimuli are dependent on the materials present; the monomethylhydrazine/material interactions under simultaneous thermal and shock stimuli are not so severe as to result in explosive decomposition at the temperature levels investigated.

4. Effect of the MMH Concentration on the Sensitivity of N_2H_4 to Adiabatic Compression

In order to determine the minimum quantity of monomethylhydrazine necessary to be added to hydrazine to desensitize hydrazine to adiabatic compression, a series of experiments was conducted at three concentration levels of monomethylhydrazine in hydrazine in three of the alloys. The alloys used were 304L SS, 347 SS, and 17-7PH; the concentration levels of monomethylhydrazine used were 2.5, 5 and 10 weight percent in hydrazine. The tests were conducted in the same manner as described for N_2H_4 , MMH, MHF-5 and MHF-7. The results obtained in 304L stainless steel tubing are presented in Table XIII.

The significant item to be noted from the data is that, while hydrazine itself is sensitive to adiabatic compression with initial propellant temperatures as low as 195°F with 2000 psig driving pressure, the addition of MMH at the 2.5 and 10 percent level raises the allowable initial propellant temperature to 400°F before sensitivity to adiabatic compression occurs, an increase of greater than 200°F. The tubes which exploded in the bath at approximately 450°F prior to testing indicate that the blends are thermally unstable at this temperature level. It should also be noted that decreasing the driving pressure from 2000 psig to 1500 psig does increase the threshold temperature limit of hydrazine from approximately 195 to 212°F.

II, B, U-Tube Adiabatic Compression Tests (cont.)

TABLE XIII

DATA INDICATIVE OF THE SENSITIVITY OF HYDRAZINE AND
HYDRAZINE/MONOMETHYLHYDRAZINE BLENDS TO ADIABATIC COMPRESSION IN
304L STAINLESS STEEL

<u>Propellant Composition</u>		<u>Temperature, °F</u>	<u>Driving Pressure, psig</u>	<u>Results</u>
<u>Hydrazine W/O</u>	<u>MMH W/O</u>			
100	-	212	2000	+,+
100	-	200	2000	+
100	-	190	2000	-, -
100	-	195	2000	+, -
100	-	200	1500	-
100	-	212	1500	+, -
90	10	212	2000	-, -
90	10	300	2000	-
90	10	400	3000	+, -, -
90	10	425	3000	+, -, -
90	10	440	3000	-
90	10	450	Exploded in bath	
95	5	212	2000	-, -
97.5	2.5	212	2000	-, -
97.5	2.5	300	2000	-, -
97.5	2.5	400	2500	-, -
97.5	2.5	400	2800	-
97.5	2.5	400	3000	+, -, -
97.5	2.5	440	Exploded in bath	
97.5	2.5	450	Exploded in bath	

The results obtained with 347 stainless steel are presented in Table XIV.

The significant item to be noted from the data is that, while hydrazine itself is sensitive to adiabatic compression with initial propellant temperatures as low as approximately 200°F in 347 stainless steel with 2000 psig driving pressure, the addition of MMH at the 2.5, 5 and 10 percent level raises the allowable initial propellant temperature to 425°F, an increase of greater than 200°F. Increasing the driving pressure from 2000 to 3000 psig does cause the blends to become sensitive to adiabatic compression at the 425°F level.

TABLE XIV

DATA INDICATIVE OF THE SENSITIVITY OF MMH/N₂H₄ BLENDS TO
ADIABATIC COMPRESSION IN 347 STAINLESS STEEL

Propellant Composition		Temperature, °F	Driving Pressure, psig	Results
Hydrazine W/O	MMH W/O			
100	-	212	2000	+,+,-
100	-	206	2000	+
90	10	350	2000	-,-
90	10	300	3000	-,-
90	10	425	2000	-,-
90	10	425	3000	+
95	5	350	2000	-,-
95	5	400	2000	-
95	5	425	2000	-,-
97.5	2.5	350	2000	-
97.5	2.5	375	2000	-
97.5	2.5	400	2000	-
97.5	2.5	425	2000	-,-
97.5	2.5	425	3000	+

The results obtained with 17-7PH stainless steel are presented in Table XV.

TABLE XV

DATA INDICATIVE OF THE SENSITIVITY OF MMH/N₂H₄ BLENDS TO
ADIABATIC COMPRESSION IN 17-7PH STAINLESS STEEL

Propellant Composition		Temperature, °F	Driving Pressure, psig	Results
Hydrazine W/O	MMH W/O			
100	-	136	2000	-
100	-	134	2000	-
100	-	132	2000	+
100	-	124	2000	-
90	10	300	2000	-,-,-
90	10	325	2000	-
90	10	350	2000	+, -
95	5	240	2000	-,-,-,-
95	5	250	2000	-,-,+
95	5	275	2000	-,+
95	5	300	2000	+, -
97.5	2.5	225	2000	-,-,-,-
97.5	2.5	240	2000	+, -
97.5	2.5	250	2000	+

II, B, U-Tube Adiabatic Compression Tests (cont.)

The significant items to be noted from the data are that, with 2000 psig driving pressure in 17-7PH stainless steel, 2.5, 5 and 10 weight percent monomethylhydrazine in hydrazine increases the threshold temperature limit of sensitivity to at least 225, 240 and 325°F, respectively. Again, a very significant increase in the desensitization of hydrazine to adiabatic compression is accomplished by the addition of as little as 2.5 weight percent monomethylhydrazine.

In summation, the 10 weight percent monomethylhydrazine in hydrazine increases the threshold temperature limit of sensitivity of hydrazine to adiabatic compression more than 200°F with all the alloys tested; 5 weight percent monomethylhydrazine in hydrazine increases that limit from 110 to greater than 200°F, depending on the alloy; and 2.5 weight percent monomethylhydrazine in hydrazine increases that limit from 95 to greater than 200°F, depending on the alloy. The increased stability due to the presence of monomethylhydrazine is significant in all cases tested.

C. THERMAL STABILITY TESTS

The thermal stability of hydrazine, monomethylhydrazine, MHF-5, and MHF-7 was measured in thermal stability bombs fabricated from 304L, 316, 321, 347, and 17-7PH stainless steel; Inconel-X, Haynes-25, and Hastelloy-X. The thermal stability in 1100-0, 6061-T6, and 2014-T6 aluminum was not determined with all of the propellant/material combinations because the aluminum bombs were so soft that they could not be resealed after several tests were made. The 1100-0 aluminum bomb was destroyed by a detonation of a hydrazine sample.

1. Apparatus and Procedures

The tests were performed according to the procedure specified in Liquid Propellant Test Methods, Test No. 6, Thermal Stability Tests, December 1969. A photograph of the Wood's metal bath and the sample bomb is shown in Figure 4. The temperature rise-rate was controlled by means of a constant rate temperature controller and two autotransformers. The bath temperature and the differential temperature between the bath and the propellant sample were measured by means of shielded-junction chromel-alumel thermocouples, and the data were recorded on a strip chart recorder.

A temperature rise rate of $10^{\circ}\text{F} \pm 2^{\circ}\text{F}/\text{minute}$ was used throughout these tests in order to avoid long periods of exposure at temperatures below those at which auto-decomposition becomes significant. All tests were started at 375 to 400°F for N_2H_4 , MMH and MHF-7 and 300 to 325°F for MHF-5. This reduced development of pressure in the sample bomb at the lower temperature where self-heating is not significant.

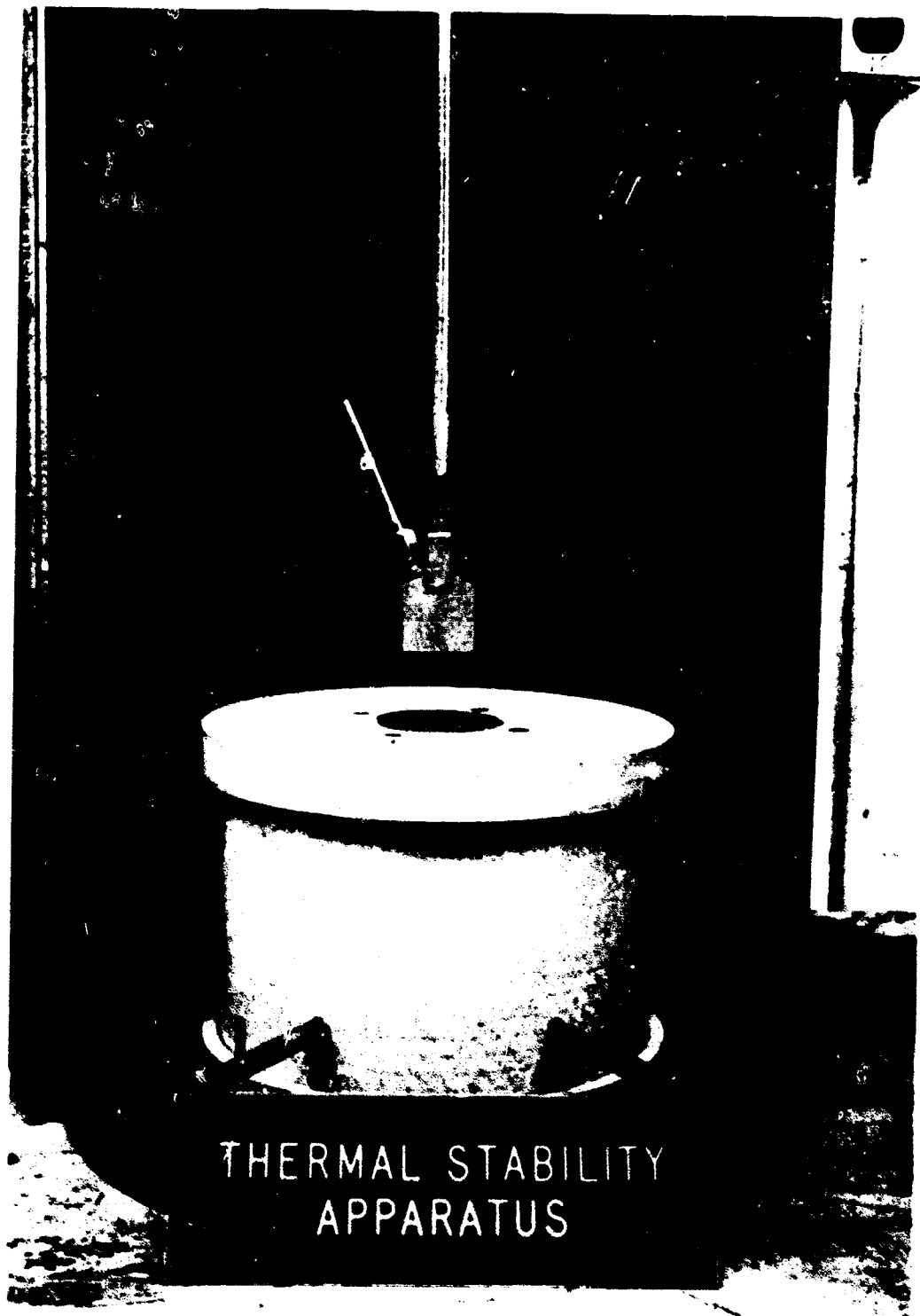


Figure 4. Thermal Stability Test Apparatus

II, C, Thermal Stability Tests (cont.)

Except in those tests to determine the effect of various impurities on the thermal stability of propellants, all propellant samples were maintained under a nitrogen atmosphere, and the sample bombs were filled and sealed in a nitrogen-purged glove-box. Preliminary tests showed that a sample size of 0.5 ml and a burst disc strength of 5300 psi were suitable for testing liquid samples.

2. Experimental Results

a. The Effect of Metals on the Thermal Stability of Hydrazine

The results of thermal stability testing of hydrazine with the various materials of construction are summarized in Table XVI. From these data it can be seen that, for most of the materials, the exotherm began at 450°F or above and that the burst discs ruptured above 500°F. However, 316 SS exhibits exotherms as low as 400°F and Hastelloy-X exhibits exotherms as low as 385°F. In the case of 321 SS and Inconel-X, which appear to be the best materials, the exotherms did not occur until 485°F although the burst disc ruptured in the vicinity of 530°F. In the case of the various aluminum bombs, it appears that the temperature at which the exotherm occurs is as low as 410°F and that the burst disc rupture occurred at temperatures in the vicinity of 500°F. One bomb, 1100-0 Al, was destroyed by the detonation of a hydrazine sample at 500°F. It is not known whether this detonation was unique or whether similar detonations occurred in other bombs but were not apparent because of the greater strength of the other materials of construction. The chemist performing the thermal stability test did note that a small number, approximately 5%, of the tests made a perceptively louder report when the burst disc ruptured. This might have been caused by a higher-order detonation of the sample.

b. The Effect of Metals on the Thermal Stability of Monomethylhydrazine

The results of thermal stability testing of MMH with the various materials of construction are summarized in Table XVII.

From the data in this table, it is apparent that Hastelloy-X is the most suitable alloy for use with monomethylhydrazine. The 304L, 316, 321, 347, and 17-7PH stainless steel, Inconel-X, and Haynes-25 all show an exotherm initiating within the range from 430 to 460°F; the burst discs all ruptured at temperatures above 520°F except for the Inconel-X. Monomethylhydrazine exhibits a lesser degree of thermal stability in the aluminum alloys than with the other materials.

TABLE XVI

DATA INDICATIVE OF THE THERMAL STABILITY OF HYDRAZINE
IN SELECTED MATERIALS

<u>Material</u>	<u>Sample Temperature Range at Which Exotherms Were Initiated, °F</u>	<u>Bath Temperatures at Which Burst Disc Ruptured, °F</u>
304L SS	450 - 460	520 - 530
316 SS	400 - 420	570 - 580
321 SS	485 - 495	530 - 560
347 SS	460	530 - 535
17-7PH	465 - 475	535 - 540
Inconel-X	490 - 495	535 - 540
Haynes-25	485	530 - 535
Hastelloy-X	385 - 420	510 - 545
2014-T6 Al	440	525 - 550
6061-T6 Al	410	502
1100-O Al	--	500 Detonation

TABLE XVII

DATA INDICATIVE OF THE THERMAL STABILITY OF MONOMETHYLHYDRAZINE
IN SELECTED MATERIALS

<u>Material</u>	<u>Sample Temperature Range at Which Exotherms Were Initiated, °F</u>	<u>Bath Temperatures at Which Burst Disc Ruptured, °F</u>
304L SS	450 - 455	535 - 530
316 SS	435 - 445	540 - 570
321 SS	435 - 460	525 - 545
347 SS	450 - 455	530 - 540
17-7PH	455	540 - 545
Inconel-X	430 - 445	500
Haynes-25	435	520 - 525
Hastelloy-X	475 - 495	525 - 565
2014-T6	390	530
6061-T6	385	450

II, C, Thermal Stability Tests (cont.)

c. The Effect of Metals on the Thermal Stability of MHF-7

The results of thermal stability testing of MHF-7 in bombs fabricated from the various materials of construction are presented in Table XVIII.

TABLE XVIII

DATA INDICATIVE OF THE THERMAL STABILITY OF MHF-7
IN SELECTED MATERIALS

<u>Material</u>	<u>Sample Temperature Range at Which Exotherms Were Initiated, °F</u>	<u>Bath Temperatures at Which Burst Disc Ruptured, °F</u>
304L SS	445 - 480	535 - 575
316 SS	495 - 505	605 - 615
321 SS	490 - 510	590 - 610
347 SS	450 - 455	540 - 550
17-7PH	450 - 465	555 - 587 (Max Exotherm)
Inconel-X	410 - 420	490
Haynes-25	450 - 470	525 - 530
Hastelloy-X	525 - 550	520 - 580
2014-T6 Al	375	484 (Max Exotherm)

The data in this table indicate that MHF-7 is most compatible with Hastelloy-X with respect to initiation of the exotherm; 316 and 321 SS are next in compatibility; 304L, 347 SS, 17-7PH, and Haynes-25 rank together as slightly less compatible; Inconel-X exhibits a still lesser degree of stability; and finally, the aluminum alloy appears to be the least compatible with the MHF-7. The 1100-O and 6061-T6 aluminum bombs were destroyed in previous testing and were not available for testing with MHF-7.

d. The Effect of Metals on the Thermal Stability of MHF-5

The results of thermal stability testing of MHF-5 with the various materials of construction are summarized in Table XIX.

II, C, Thermal Stability Tests (cont.)

TABLE XIXDATA INDICATIVE OF THE THERMAL STABILITY OF MHF-5
IN SELECTED MATERIALS

<u>Material</u>	<u>Sample Temperature Range at Which Exotherms Were Initiated, °F</u>	<u>Bath Temperatures at Which Burst Disc Ruptured, °F</u>
304L SS	355 - 390	425 - 455
316 SS	300 - 330	475 - 495
321 SS	340 - 350	425 - 430
347 SS	355	450 - 465
17-7PH	355	440 - 460
Inconel-X	290 - 300	455
Haynes-25	325 - 360	435 - 455
Hastelloy-X	350 - 365	460 - 485
6061-T6 Al	375	400

These data show that the MHF-5 is much less stable than the other propellants. The aluminum alloy exhibits the greatest degree of compatibility with MHF-5 of the materials listed. The next level of compatibility occurs with 304L SS, 321 SS, 347 SS, 17-7PH, and Hastelloy-X. Haynes-25 is only slightly less compatible and, finally, 316 SS and Inconel-X appear to be the least compatible with MHF-5 of all the materials investigated.

e. The effect of Impurities on the Thermal
Stability of Hydrazine

Several tests were conducted in 304L SS bombs to determine the effect of air and CO₂ on the thermal stability of hydrazine. The results of these tests are presented in Table XX.

These data show that the presence of air slightly reduces the thermal stability below that of hydrazine under a nitrogen atmosphere. The addition of water and CO₂ appear to have no effect over the concentration range investigated.

II, C, Thermal Stability Tests (cont.)

TABLE XX

THE EFFECT OF IMPURITIES ON THE THERMAL STABILITY OF HYDRAZINE

<u>Sample Description</u>	<u>Sample Temperatures at Which Exotherms Were Initiated, °F</u>	<u>Bath Temperatures at Which Burst Disc Ruptured, °F</u>
0.5 cc liquid, air ullage	440	520
	430	522
	415	501
0.5 cc liquid, N ₂ ullage	450	528
	450	520
0.5 cc liquid, N ₂ ullage; H ₂ O added to correspond to 98% N ₂ H ₄ /2% H ₂ O	460	530
0.5 cc liquid, air ullage; 50 ppm CO ₂ added to N ₂ H ₄	470	525

A series of thermal stability tests was conducted at elevated temperatures in which only N₂H₄ or MMH vapors were present in a 304L SS thermal stability bomb. The data from these tests, reported in Table XXI, show that the results are extremely erratic and that, in those tests in which the burst discs were ruptured, the rupture occurred at temperatures nearly 100°F below that at which the rupture occurred in those tests where liquid was present.

TABLE XXI

THE THERMAL STABILITY OF N₂H₄ AND MMH VAPORS IN 304L STAINLESS STEEL

<u>Sample Description</u>	<u>Sample Temperatures at Which Exotherms Were Initiated, °F</u>	<u>Bath Temperatures at Which Burst Disc Ruptured, °F</u>
25μl N ₂ H ₄ , N ₂ ullage	455	--
	395	--
	--	442
	420,430	455
40μl MMH, N ₂ ullage	390,430	454
	420	--
	445	--
	--	434

II, C, Thermal Stability Tests (cont.)

It should also be noted that the report accompanying the rupture seemed louder than that which occurred with those tests where liquid was present. From this, it would appear that the presence of a liquid phase has a "quenching" effect on N_2H_4 and MMH vapors.

3. Summation of Results

Based on the temperatures at which the exotherms are initiated in the presence of a liquid phase, the thermal stability of the fuels increases with the materials investigated in the following order:

Hydrazine: Hastelloy-X < 316, 6061-T6 < 2014-T6 < 304L, 347,
17-7PH < Haynes-25 < 321, Inconel-X

Monomethylhydrazine: 6061-T6, 2014-T6 < Haynes-25, Inconel-X,
316, 321 < 347, 17-7PH, 304L < Hastelloy-X

MHF-7: 2014-T6 Inconel-X < 347, 304L, 17-7PH, Haynes-25 < 321,
316 < Hastelloy-X

MHF-5: Inconel-X < 321 < 347, 17-7PH, 304L, Hastelloy-X, < 2014-T6
< 316 < Haynes-25

The thermal stabilities of hydrazine, monomethylhydrazine, and MHF-7 in the stainless steels are very similar, but the explosive decomposition of MHF-7 occurs at a higher temperature than for hydrazine or monomethylhydrazine. The explosive decomposition reactions do not occur until the temperature of the fuels is above 500°F. The thermal stability of MHF-5 is significantly less than that of the other fuels; this can be attributed to the presence of the nitrate radical in MHF-5.

Hastelloy-X appears to be superior to the stainless steels in the presence of MMH, MHF-5 and MHF-7. Haynes-25 behaves similarly to the stainless steels, while Inconel-X exhibits significantly more reactivity with monomethylhydrazine, MHF-7 and MHF-5 than do the stainless steels. The aluminum alloys initiate exothermic decomposition of the hydrazine, monomethylhydrazine and MHF-7 at temperatures significantly lower than the other alloys.

The activation energies for the decomposition of the propellant in the various materials of construction were calculated from the thermal stability test data using the procedure in Liquid Propellant Test Methods,

II, C, Thermal Stability Tests (cont.)

Test No. 6, Thermal Stability Tests, December 1959. The results of these calculations, tabulated in Table XXII, show that, in general, hydrazine has the lowest activation energy, 20 to 30 kcal/mole; MHF-5 is slightly higher with activation energies in the range of 25 to 35 kcal/mole. The activation energies for MMH range from 31.5 to 66.9 kcal/mole and from 33 to 63.5 kcal/mole for MHF-7.

TABLE XXII

ACTIVATION ENERGIES FOR FUEL DECOMPOSITION
DERIVED FROM THERMAL STABILITY MEASUREMENTS

<u>Material</u>	<u>N₂H₄</u>	<u>MMH</u>	<u>MHF-5</u>	<u>MHF-7</u>
304L SS	26.8	66.9	35.5	63.5
316 SS	21.0	36.0	28.0	56.0
321 SS	24.0	36.5	32.6	33.0
347 SS	~20.0	46.6 46.9	24.0	49.8 47.0
17-7PH	22.0	31.5	32.6	43.2
Inconel-X	25.6	>60.0	32.3	60.0
Haynes-25	28.5	52.3	24.0	46.6
Hastelloy-X	30.0	36.0	32.0	49.0

The activation energy values obtained with hydrazine are reasonable in view of the approximation method used and are consistent with a heterogeneous decomposition mechanism. The values obtained with MHF-5 also appear to possess some validity. However, the scatter in the activation energy values for the decomposition of monomethylhydrazine and MHF-7 casts some doubt on the validity of values, particularly those in the 60 kcal/mole range. The values in the 30 to 40 kcal/mole range are consistent with a heterogeneous decomposition mechanism for monomethylhydrazine; the values in the 60 kcal/mole range correspond to N-N bond scission in a homogeneous mechanism (Ref 2) which is not consistent with other results obtained during this test series.

D. DETONATION PROPAGATION TESTS

The purpose of the detonation tests is to determine the sensitivity of various combinations of material and the liquid phase of the propellants to thermal and shock stimuli. The test evaluates the critical diameter for propagation of a detonation wave, and the maximum diameter value evaluated

II, D, Detonation Propagation Tests (cont.)

is one inch. The discussion in this section is presented under two headings: (1) Apparatus and Procedures and (2) Experimental Results.

1. Apparatus and Procedures

The basic apparatus and procedures are described in the "Liquid Propellant Test Methods, Test No. 8, Critical Diameter and Detonation Velocity Test, May 1964." The standard test equipment and procedures were developed for use at ambient temperatures, $70 \pm 10^\circ\text{F}$; therefore, some modifications were necessary in order to conduct the tests at elevated temperatures, $>100^\circ\text{F}$.

A schematic diagram of the apparatus used for the tests described below is shown in Figure 5; a photograph of the apparatus is shown in Figure 6; and a photograph of a sample tube is shown in Figure 7. Because of the temperature level anticipated during the tests, $\sim 400^\circ\text{F}$, the sample tube must be sealed to avoid evaporation of the propellant and a provision must be made to allow for liquid expansion due to the significant change in liquid densities during heating. The sample tube was sealed at the top by welding a 5 to 10 mil 304L stainless steel disc over the tube end. The other end was closed by welding a 304L stainless steel plate which contained a 1/8-inch AN fitting to the tube. The heated liquid was allowed to expand through a 1/8-inch line into a reservoir pressurized with nitrogen to a value exceeding the anticipated vapor pressure value of the propellant at the selected temperature.

The blasting cap and Pentolite booster charge (50 gm) were positioned approximately three inches above the top of the sample tube so that the Pentolite would not undergo thermal decomposition during the heating cycle. The blasting cap and Pentolite booster charge were dropped onto the top of the sample tube immediately prior to testing by a remotely operated solenoid.

The heater was fabricated by firmly attaching two 1350-watt electric-resistance heating plates to a 2-inch aluminum tube approximately 36 inches long. The tube was made with a slot so that the 1/8-inch line would not interfere with the dropping of the heater prior to the detonation.

The heater tube dropped through a hole which was covered during the detonation by a heavy aluminum plate. This prevented the destruction of a heater with each test. The cover plate also moved in the opposite direction initially to effect the dropping of the heater tube through the hole; the heater was positioned on the edge of the cover plate. The heater was concentrically maintained in place around the sample tube by inserting a small amount of glass wool in the annulus between the heater and the tube.

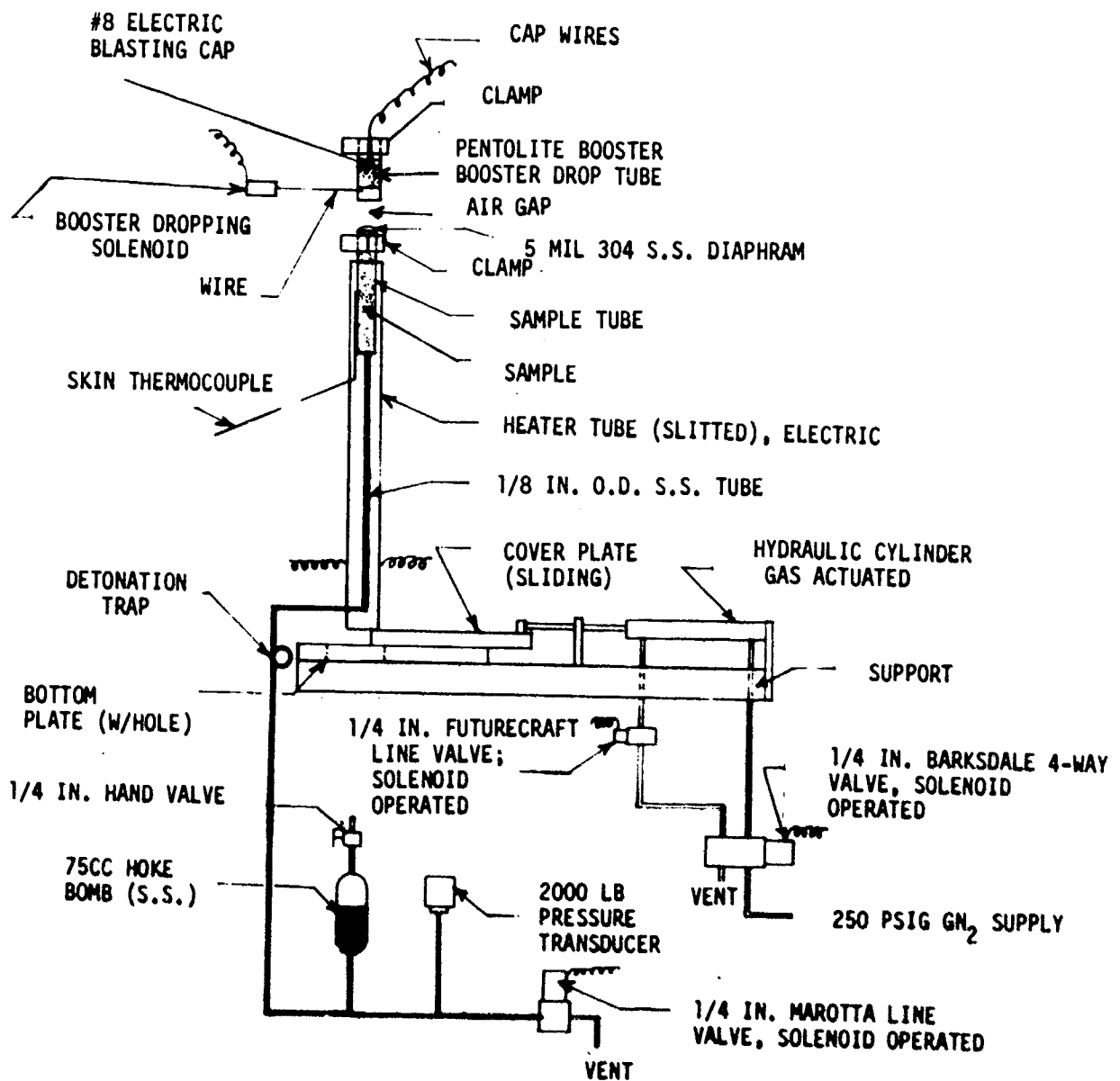


Figure 5. Schematic Diagram of Detonation Propagation Test Apparatus

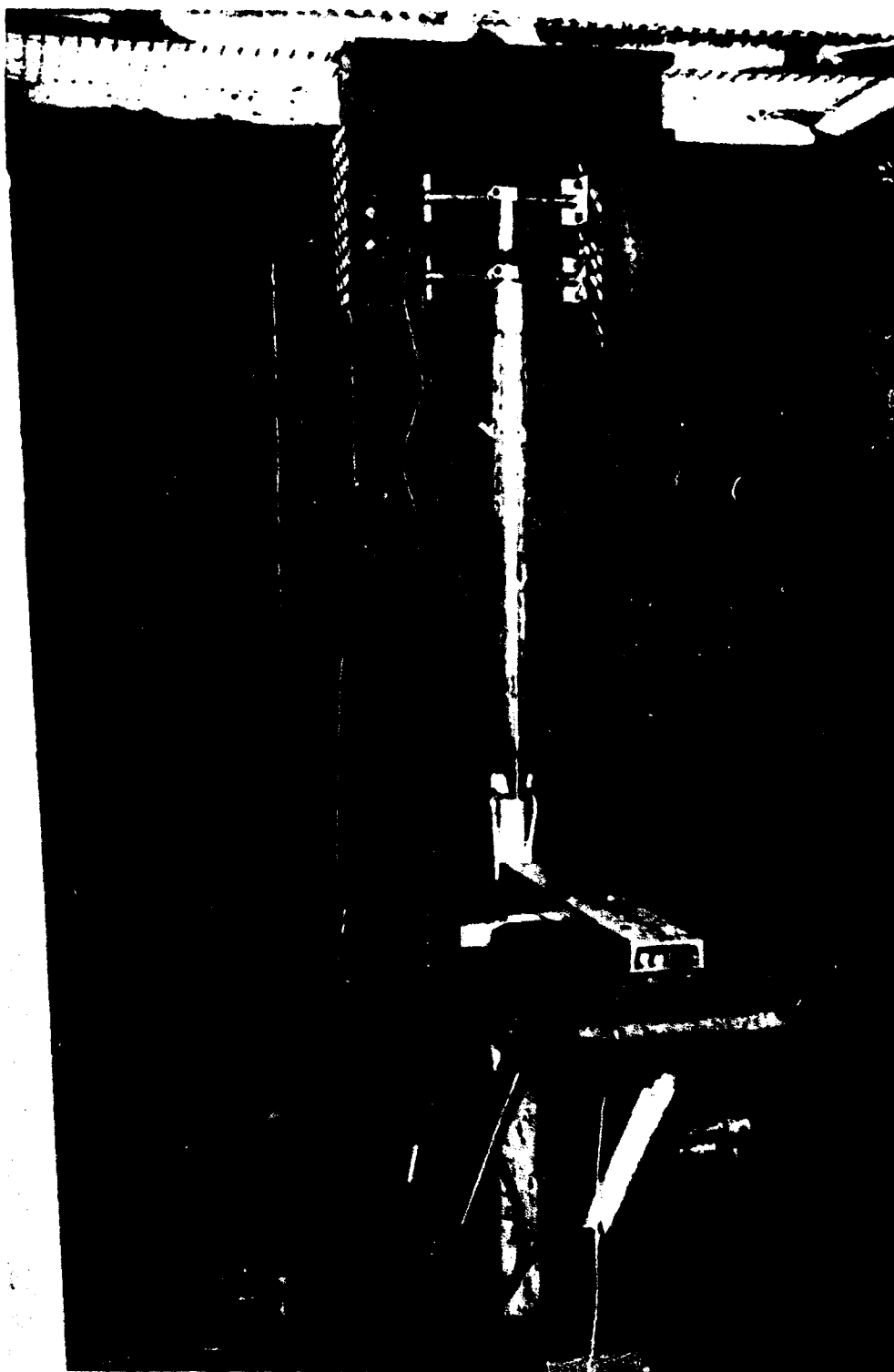


Figure 6. Detonation Propagation Test Apparatus



Figure 7. Sample Tube Used for Detonation Propagation Testing

II, D, Detonation Propagation Tests (cont.)

The temperature of the sample under test was measured by means of a thermocouple welded to the surface of the sample tube. Tests were conducted in which thermocouples were positioned on the surface of the sample tube and in the liquid inside the tube. The inner thermocouple was within 7°F of the outer thermocouple valve throughout the temperature range. The 7°F correction was applied to all the skin thermocouple readings. The temperature values are reported as that of the liquid.

The typical test procedure used is as follows: The sample tube components were thoroughly cleaned prior to welding with a tungsten inert gas (TIG) welding apparatus using argon as the cover gas during the welding operation. The sample tube was then filled with a 50% aqueous hydrazine solution and passivated for at least 16 hours. After the passivation, the tube was thoroughly rinsed with distilled water and then placed in an oven until nearly dry. The last traces of water were removed by subjecting the tubes to a vacuum of 10 microns; the tubes were then filled with dry nitrogen and capped until used.

The sample tube was filled with the propellant (~80 ml) by means of a hypodermic syringe and capped. This operation was conducted in a nitrogen atmosphere. The sample tube was then placed in position in the test apparatus. The liquid expansion reservoir and connecting 1/8-inch line were filled with the propellant so that 30 ml of ullage remained in the reservoir. The sample tube was uncapped and the filled 1/8-inch line attached to the sample tube. The reservoir was then pressurized to at least 200 psig with nitrogen. (As the liquid expanded in the sample tube, the pressure increased sufficiently in the ullage to maintain a pressure level above the vapor pressure of the propellant.) The heater was then positioned on the edge of the sliding cover and the glass wool inserted at the top of the heater in the annulus.

The Pentolite booster charge was then placed in position with the attached blasting cap. The dropping mechanism was operated manually to ensure that the charge would drop in place, and then the charge was repositioned. The electric blasting cap was then connected to the proper terminals located outside of the protective cage. The heater was then energized from a remote location and the blasting cap device was armed. The temperature and pressure were monitored from the control room and, as the desired temperature was attained, the heater was dropped and the protective cover closed. The blasting cap and booster charge were dropped on the top of the sample tube, and the blasting cap was activated.

The criterion for a positive test as specified by Test Method No. 8 is "the length of the tubing containing the donor section, i.e., the forerunning section (5 inches) should be completely destroyed and reduced to fine fragments. In the critical diameter tests, the tubing under test will

II, D, Detonation Propagation Tests (cont.)

be completely fragmented its entire length (30 inches) if it is greater than critical diameter or fragmented for only a short distance if it is less than critical diameter."

2. Experimental Results

The detonation propagation tests were conducted with four materials: 304L and 347 stainless steels, Inconel-X, and Haynes-25; the propellants tested were limited to hydrazine and MHF-5, except for one test with monomethylhydrazine. The aluminum alloys were not used in the test series because of their lack of structural strength at the elevated temperatures. MHF-7 was not used in this test series, and only one test was conducted with monomethylhydrazine because of the demonstrated stability of monomethylhydrazine in the adiabatic compression and thermal stability tests and because monomethylhydrazine is the major component of MHF-5. Unless a detonation is propagated in liquid MHF-5, the testing of monomethylhydrazine itself is not warranted.

The upper limit of the temperatures used in the tests was based on the results from the thermal stability tests. The temperatures of the liquids in the tests are below the temperatures at which exotherms were initiated in the thermal stability tests. The results obtained from tests are presented in Table XXIII. The sample tubes were one inch diameter (0.9-inch ID) and 8 inches long unless specified otherwise in the table.

The data from Table XXIII indicate that, within the range of elevated temperatures tested, liquid hydrazine, monomethylhydrazine, and MHF-5 will not propagate a detonation in 0.9-inch internal diameter tubes. The MHF-5 was not tested at temperatures above 350°F because the earlier thermal stability tests indicate that an exothermic decomposition reaction is initiated at this temperature level. The result obtained in the test with 304L SS and hydrazine at 422°F (i.e., the hydrazine exploded prior to triggering the detonation device) may have been caused by a vapor phase reaction. (In two tests, the thin metal diaphragm on the tube ruptured during the heating cycle prior to the detonation. The temperatures at which the rupture occurred were 316 and 343°F with hydrazine as the fuel.) Data from thermal stability tests with only hydrazine vapor present indicate that the explosive decomposition of the vapor occurs in the vicinity of 400°F. In the test at 400°F with hydrazine in 304L SS in which the tube fragmented into large pieces, it appeared that simultaneous with detonation propagation test a vapor decomposition reaction occurred. To confirm that this was the case, a subsequent test was conducted with a 1-inch-diameter tube 30 inches long and with the liquid temperature at 425°F. The detonation did not propagate in this tube.

Because all the tests with hydrazine and MHF-5 were negative, a test was conducted with a liquid known to propagate a detonation at ambient

TABLE XXIII

DATA ON DETONATION PROPAGATION TESTING OF
HYDRAZINE AND MHF-5 IN ONE-INCH-DIAMETER TUBES

<u>Material</u>	<u>Propellant</u>	<u>Liquid Temp, °F</u>	<u>Results</u>
304L SS	MHF-5	320	No propagation
304L SS	N ₂ H ₄	419	No propagation
304L SS	N ₂ H ₄	422	N ₂ H ₄ exploded before detona- tion device was triggered.
304L SS	N ₂ H ₄	400	Tube fragmented into large pieces, not a high order detonation.
304L SS	N ₂ H ₄	425	No propagation, 30-inch tube
304L SS	94% nitromethane/ 6% ethylene diamine	Ambient	Tube was pulverized, only small fragments of the "B" nut and plug were recovered, 30-inch tube.
316 SS	N ₂ H ₄	400	No propagation
316 SS	N ₂ H ₄	400	No propagation
316 SS	MHF-5	327	No propagation
316 SS	MHF-5	325	No propagation
316 SS	MMH	442	No propagation
347 SS	N ₂ H ₄	223	No propagation
347 SS	N ₂ H ₄	300	No propagation
347 SS	N ₂ H ₄	319	No propagation
347 SS	N ₂ H ₄	405	No propagation
347 SS	N ₂ H ₄	423	No propagation
347 SS	MHF-5	350	No propagation
Inconel-X	N ₂ H ₄	306	No propagation
Inconel-X	N ₂ H ₄	370	No propagation
Inconel-X	N ₂ H ₄	403	No propagation
Inconel-X	MHF-5	296	No propagation
Inconel-X	MMH	403	No propagation
Haynes-25	N ₂ H ₄	373	No propagation
Haynes-25	N ₂ H ₄	406	No propagation
Haynes-25	MHF-5	318	No propagation
Hastelloy-X	N ₂ H ₄	390	No propagation
Hastelloy-X	N ₂ H ₄	400	No propagation
Hastelloy-X	MHF-5	350	No propagation
Hastelloy-X	MHF-5	350	No propagation
Hastelloy-X	MMH	440	No propagation
Hastelloy-X	MMH	485	No propagation

II, D, Detonation Propagation Tests (cont.)

temperature--94% nitromethane/6% ethylene diamine. The results are included in the table for comparison. In this case, the 30-inch tube was completely destroyed. A photograph of the typical tubes after a negative test is shown in Figure 8. The tube at the bottom of the photograph (No. 1) contained water at 380°F; the tube at the top of the photograph (No. 6) contained MHF-5 at 350°F. The damage to the tubes is remarkably similar.

E. CONFIRMATORY TESTS

The purpose of the confirmatory tests was to establish the fact that the materials do have an effect on the temperature at which the explosive decomposition of the propellant occurs under thermal soak conditions.

A schematic diagram of the test device is shown in Figure 9, and a photograph of the device is shown in Figure 10. The apparatus consists of a 1/4-inch-diameter tube, one end of which is attached to the adiabatic-compression apparatus and the other end is sealed except for a 0.010-inch orifice. The end of the tube with the orifice is heated with an electrical resistance heater to the desired temperature level to simulate a thermal-soak situation. The temperature is measured both at the tip of the tube and underneath the resistance heater by thermocouples. Three ml of hydrazine was placed in the tube and the liquid temperature of the hydrazine was controlled by submerging the "U" portion of the device in a water bath at a selected temperature. After the desired temperature levels were attained, the valve on the adiabatic compression device was opened; the protective burst disc was ruptured; and the hydrazine was expelled through the hot orifice. The burst disc was used to prevent the condensation of the propellant in the check valve assembly. The compression process was not adiabatic due to the orifice in the end of the tube.

Hydrazine was selected as the propellant for the tests because the hydrazine vapor is the most sensitive compound of those encountered in the current investigation. The materials used were 304L and 17-7PH stainless steel because they displayed significant differences in the adiabatic compression tests with hydrazine. The driving pressure used in the tests was 1500 psig of nitrogen; this pressure level was necessary to ensure the rupture of the burst discs. The tests in which the apparatus survived intact are designated by a - sign, while tests in which the tube ruptured are designated by a + sign. The experimental results are presented in Table XXIV.

The significant item to be noted from the data is that the temperature at which the explosive decomposition of hydrazine occurs is dependent on the stainless steel in which the test is conducted. The hot spot in the 304L SS tube is greater than 950°F before the explosive decomposition occurs, while the hot spot in the 17-7PH SS tube is 700°F for the explosive decomposition to occur. Obviously, the lack of explosive decomposition of hydrazine at the high temperature encountered in this test series is governed by



Figure 8. Examples of Tubes After the Detonation Propagation Tests

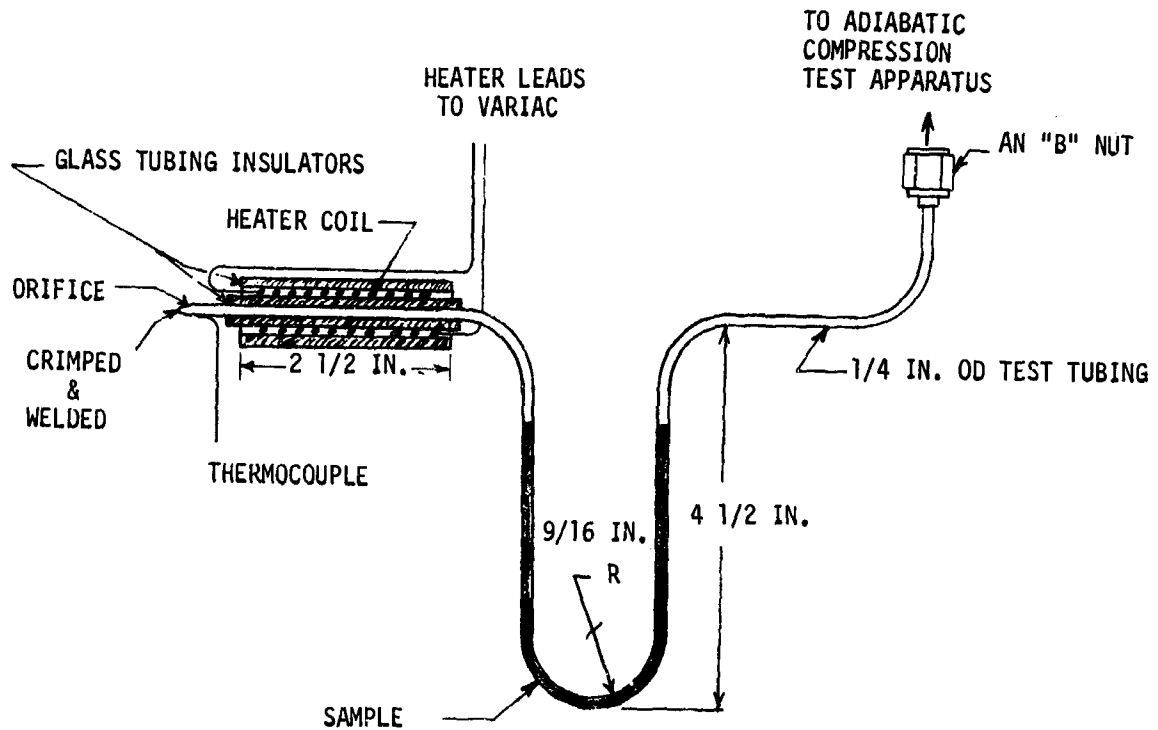


Figure 9. Schematic Diagram of Confirmatory Test Apparatus

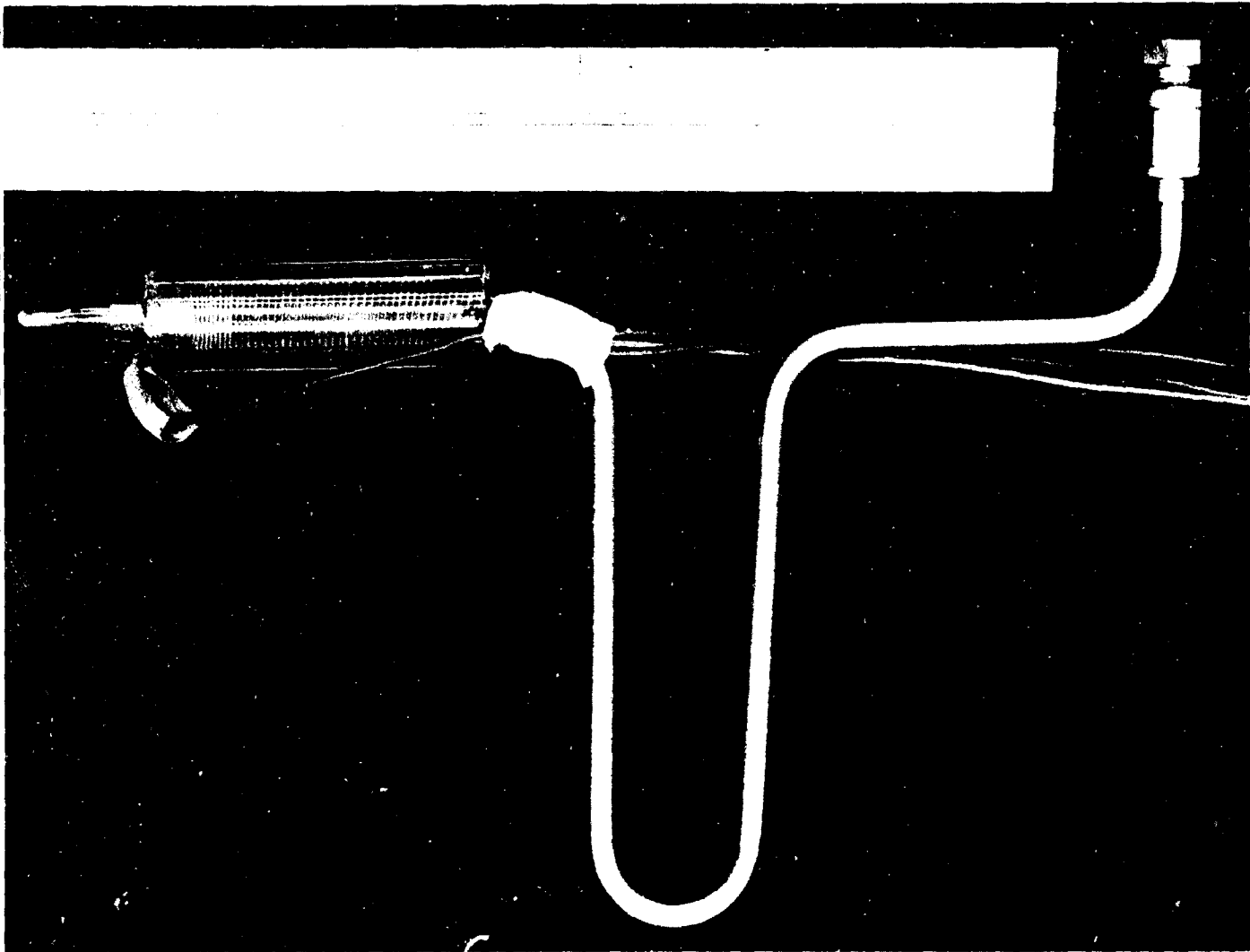


Figure 10. Confirmatory Test Apparatus

TABLE XXIV

DATA ON THE BEHAVIOR OF HYDRAZINE IN STAINLESS STEEL TUBING
DURING THERMAL SOAK CONDITIONS

<u>Type of Stainless Steel</u>	<u>Liquid N₂H₄ Temperature, °F</u>	<u>Tube Temperature, at Orifice, °F</u>	<u>Tube Temperature Under Heater, °F</u>	<u>Result</u>
304L	150	371	550	-
304L	150	428	650	-
304L	150	515	750	-
304L	150	550	808	-
304L	185	513	750	-
304L	185	550	860	-
304L	212	514	750	-
304L	212	550	850	-
304L	212	550	900	-
304L	212	550	986	+
304L	212	621	950	-
304L	212	685	1000	+
17-7PH	212	332	550	-
17-7PH	212	385	650	-
17-7PH	212	442	750	+
17-7PH	212	540	700	+
17-7PH	212	413	650	-
17-7PH	212	468	700	+

II, E, Confirmatory Tests (cont.)

the rate of heat transfer to the hydrazine as it passes through the relatively "hot" sections of the device. The standard tests have adequately demonstrated that the temperature of the bulk liquid hydrazine cannot approach the "hot spot" temperatures encountered in this device without undergoing explosive decomposition. The confirmatory tests are only intended to demonstrate that the material of construction is an important factor in initiating the explosive decomposition of the propellant at elevated temperatures.

F. IMPLICATIONS OF THE EXPERIMENTAL RESULTS

The adiabatic compression test is a method for evaluating the sensitivity of liquid monopropellants to initiation of decomposition due to the rapid compression of gas bubbles. The rapid compression may result from mechanical shock to containers of fuel or from the rapid closing of valves in propellant lines containing the entrained gas bubbles. The data from this program indicate that, under the most severe conditions, the decomposition of monomethylhydrazine, MHF-7, or MHF-5 in the presence of stainless steels and Inconel-X will not be explosive at liquid temperatures up to 400°F and, in Haynes-25, only MHF-5 may decompose explosively at temperatures above 385°F while the monomethylhydrazine and MHF-7 behave similarly as in the stainless steels.

In the case of hydrazine itself, however, the temperature limits are much more severe. With the 304L, 316, 321 and 347 stainless steels, Hastelloy-X, and Haynes-25, the explosive decomposition is not initiated if the temperature of the liquids is maintained below 200°F; with 17-7PH and Inconel-X, this temperature value drops to 130°F; and with the 6061-T6 and 2014-T6 aluminum alloys, the decomposition can be initiated at ambient temperatures.

The detonation propagation tests demonstrated that, even though a detonation occurs, it will not be propagated in the liquid phase if the diameter of the tubing is restricted to 0.9 inch internal diameter or less at initial liquid temperatures approaching the regime in which thermal decomposition becomes significant. However, the possibility of a detonation in hydrazine vapor itself at much lower temperatures is very real.

The thermal stability tests provide a temperature limit which should not be exceeded in the liquid propellants if significant decomposition is to be avoided. The tests also provide a temperature value at which the decompositions become explosive. With hydrazine, monomethylhydrazine, and MHF-7, significant exothermic decomposition occurs between 400 and 500°F in all the materials investigated; with MHF-5, the corresponding decomposition occurs between 300 and 400°F. Above these temperature levels, the decomposition becomes explosive.

II, F, Implications of the Experimental Results (cont.)

The confirmatory tests very approximately simulated a restart under thermal soak conditions and demonstrated that "hot spots" in a system do not inevitably lead to catastrophic failure if the heat transfer rate is properly limited.

The results from the adiabatic compression tests, the thermal stability test, and the confirmatory tests all indicate that there is a material/propellant interaction under the test conditions and that proper selection of metal alloys can provide an additional margin of safety in the design of propulsion systems. In addition, the test data demonstrated the effectiveness of monomethylhydrazine vapor in "quenching" the explosive decomposition behavior of the hydrazine vapor. All the results of the tests are based on the use of properly cleaned and adequately passivated materials.

SECTION III

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The following conclusions may be drawn from the experimental program:

1. Based on the thermal stability tests, the self-heating of N_2H_4 due to exothermic decomposition does not become appreciable until the temperature reaches 400°F or above in 304L, 316, 321, 347, and 17-7PH stainless steels, Inconel-X, Haynes-25, Hastelloy-X, and 2014-T6 and 6061-T6 aluminums. For monomethylhydrazine, the same is true except that an exotherm is detected at 385°F in 6061-T6 aluminum; MHF-7 is similar except that an exotherm occurs at 375°F in 2014-T6 aluminum. The self-heating of MHF-5 becomes apparent at 340°F or above in the alloys except for Inconel-X in which an exotherm is initiated at approximately 290°F, Haynes-25 with an exotherm as low as 325°F, and 316 SS with an exotherm as low as 300°F. Decomposition of the propellants occurs at temperatures below the levels reported, but the rate is not sufficient to produce self-heating in the apparatus.

2. Hydrazine and monomethylhydrazine will not propagate a detonation in the liquid phase in 0.9-inch internal diameter tubes at temperatures up to at least 400°F; the same is true of MHF-5 at temperatures up to 325°F.

3. Hydrazine is sensitive to adiabatic compression at temperatures below 100°F in aluminum alloys, at 130°F in Inconel-X and 17-7PH, and between 200 to 218°F in 304L, 316, 321, and 347 stainless steels, Hastelloy-X, and Haynes-25. Monomethylhydrazine and MHF-7 are not sensitive to adiabatic compression at temperature levels as high as 520°F; for MHF-5, the sensitivity to adiabatic compression occurs at temperatures at which the explosive decomposition occurs in the thermal stability tests.

4. Monomethylhydrazine has a "quenching" effect on the explosive decomposition of hydrazine vapors at temperatures below 425°F at concentration levels as low as 2.5 weight percent in hydrazine.

5. As a generalization, Hastelloy-X exhibits excellent propellant/material compatibility characteristics with MMH, MHF-5, and MHF-7 in comparison to the other alloys investigated but is inferior with hydrazine in the thermal stability test.

6. The evaluation procedures used in the program provide a reliable means to define potential propellant/material interactions under simultaneous thermal and shock stimuli.

III, Conclusions and Recommendations (cont.)

B. RECOMMENDATIONS

1. To minimize the detonation hazard with hydrazine vapor, small quantities of monomethylhydrazine should be added to the hydrazine. As little as 2.5 weight percent monomethylhydrazine in hydrazine provides a significant improvement in diminishing the sensitivity to adiabatic compression. The minimum quantity of monomethylhydrazine which is necessary to desensitize hydrazine vapor has not been established for special applications; the lower limit warrants investigation.
2. The use of ammonia as a desensitizing agent for the detonation of hydrazine vapor under adiabatic conditions should be investigated.
3. New monopropellant and monopropellant blends should be subjected to the evaluation tests used in this program prior to extensive development. The baseline data obtained with hydrazine provide a standard of comparison for the new monopropellant candidates.
4. The use of other metal alloys with the propellants used in this study or the use of metal alloys with new monopropellants warrant investigation by the propellant characterization procedures before extensive development is initiated.
5. Aluminum itself should be more extensively investigated in modified test apparatus which compensate for the lack of structural strength of the aluminum itself.

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APPENDIX

COMPOSITIONS OF THE ALLOYS USED IN THE INVESTIGATION

Report AFRPL-TR-71-41, Appendix

TABLE A-I

NOMINAL COMPOSITIONS OF THE STAINLESS STEEL ALLOYS
COMPOSITION, PERCENT

<u>Element</u>	<u>304L</u>	<u>316</u>	<u>321</u>	<u>347</u>	<u>17-7PH</u>
Fe	Remainder	Remainder	Remainder	Remainder	Remainder
C	0.026	0.06	0.037	0.04	0.06
Mn	1.63	1.45	1.43	0.98	0.60
P	0.013	0.019	0.019	0.025	0.023
S	0.009	0.02	0.01	0.010	0.019
Si	0.58	0.46	0.54	0.66	0.46
Ni	10.11	12.72	11.74	9.48	7.05
Cr	18.14	16.99	17.46	18.10	17.18
Mo	--	2.39	0.24	0.19	0.08
Cu	--	--	0.36	0.20	0.19
Cb-Ta	--	--	0.17	0.83	--
Co	--	--	0.06	--	--
Al	--	--	--	--	1.08

TABLE A-II

NOMINAL COMPOSITIONS OF ALLOYS

COMPOSITION, PERCENT

<u>Element</u>	<u>Hastelloy-X</u>	<u>Haynes-25</u>	<u>Inconel-X</u>	<u>6061-T6</u>	<u>2014-T6</u>
Fe	19.06	2.26	6.77	0.7	1.0 max
C	0.09	0.09	0.03	--	--
Mn	0.65	1.55	0.51	0.15	0.4/1.2 Si
P	--	0.007	--	--	--
S	0.006	0.006	0.007	--	--
Si	0.64	0.24	0.32	0.4/0.8	0.5/1.2
Ni	Remainder	10.25	73.17	--	--
Cr	21.23	19.88	14.68	0.40/0.35	0.1 max
Cb+Ta	--	--	0.94	--	--
W	0.45	14.95	--	--	--
Cu	--	--	0.26	0.15/0.40	3.9/5.0
Co	1.41	50.79	--	--	--
Al	--	--	0.76	Remainder	Remainder
Ti	--	--	2.53	0.15	0.15 max
Mg	--	--	--	0.8/1.2	0.2/0.8
Zn	--	--	--	0.25	0.25 max
Mo	8.44	--	--	--	--
B	0.005	--	--	--	--

ABSTRACT

The objective of this program was to define the threshold sensitivity limit of hydrazine fuels in common metallic materials of construction as a function of temperature and pressure. Four propellants were included in the program: hydrazine, monomethylhydrazine, MHF-5, and MHF-7. Eleven metallic materials of construction were included in the program: stainless steel 304L, 316, 321, 347, and 17-7PH; aluminum 1100-0, 6061-T6, and 2014-T6; Inconel-X 750; Haynes-25; and Hastelloy-X. Three standard tests were used to determine the threshold sensitivity limit of the propellants in the various materials: (1) thermal stability test, (2) detonation propagation test, and (3) U-tube adiabatic compression test.

The hydrazine, monomethylhydrazine, and MHF-7 were found to possess comparable thermal stability characteristics in the stainless steels, Inconel-X, Haynes-25, and Hastelloy-X, with less stability evident in the 2014-T6 and 6061-T6 aluminum alloys. The thermal stability temperature limits for MHF-5 were approximately 100°F lower than for the other fuels.

The detonation propagation tests demonstrated that the liquid phase of the fuels does not propagate a detonation in 0.9-in. internal diameter tubes at temperatures up to 400°F in hydrazine and monomethylhydrazine and up to 325°F in MHF-5.

Propellant/material interaction was apparent in the U-tube adiabatic compression tests. Under adiabatic compression conditions, the threshold temperature limit for explosive decomposition of hydrazine was 195°F to 217°F in 347SS, Haynes-25, 316SS, 321SS, Hastelloy-X, and 304LSS. The value dropped to 130°F for Inconel-X and 17-7PH, and the value dropped to less than 100°F for 2014-T6 and 6061-T6 aluminum. Monomethylhydrazine and MHF-7 were not sensitive to adiabatic compression to temperatures of at least 500°F; MHF-5 decomposed explosively under adiabatic compression at temperature levels approaching those at which explosive decomposition occurred in the thermal stability tests. The ability of small quantities of monomethylhydrazine to desensitize hydrazine vapor to adiabatic compression was dramatically demonstrated using 347SS, 304LSS, and 17-7PH with monomethylhydrazine concentration levels ranging from 2.5 to 10 weight percent in hydrazine. In addition, some confirmatory tests were conducted under thermal soak conditions to demonstrate the effect of materials under simulated thruster conditions.

All the tests were conducted with propellant-grade fuels and the materials were cleaned and passivated prior to testing.

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